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RESEARCH

Optimal synthesis of methyl ester of Sal oil (*Shorea robusta*) using ion-exchange resin catalyst

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Abstract This paper deals with the synthesis of Sal oil methyl ester (SOME) biodiesel using Sal oil (*Shorea robusta*) and acidic ion-exchange resin catalyst (INDION-225 H). An experimental set-up was proposed for the synthesis of SOME biodiesel where esterification of free fatty acids and transesterification of glycerides of fatty acids took place simultaneously with continuous removal of water. Effects of methanol and catalyst loading were studied to maximize the conversion of Sal oil to SOME biodiesel. Biodiesel productivity was also tested using recycled catalyst and a constant yield of biodiesel was obtained for *all* the catalyst recycle experiments. Scanning electron microscope (SEM) study of recycled catalyst was carried out to check the morphology of the catalyst and the degradation of the catalyst after recycling. SEM analysis revealed that the catalyst activity remained unchanged after several recycles. In the proposed process, ion-exchange resin not only reduced catalyst consumption and effluent generation considerably but also enhanced the productivity of SOME biodiesel considerably by eliminating the steps of purification. Acid value was measured continuously to monitor the extent of biodiesel formation with reaction time. The yield of SOME biodiesel was measured after purification of the reaction mass and it was tested using ASTM's standard methods of biodiesel testing. Finally, the properties of SOME biodiesel were compared with the petroleum-based diesel fuel.

Keywords Sal oil · Ion-exchange resin · Biodiesel · Catalyst recycle · SEM · ASTM

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Introduction

As the petroleum reserves are depleting rapidly with a prediction of being totally exhausted in the near future, present day researchers have concentrated on finding the alternative fuel sources. In this regard, biodiesel may be treated as a promising alternative source of fossil fuel. Biodiesel is a biomass-based, biodegradable, non-toxic and renewable fuel that has been used in internal combustion engines successfully with reduced emission of carbon monoxide, sulphur dioxide, hydrocarbons, particulate matters, polyaromatics and smokes [1–4]. Moreover, it does not contribute any additional CO_2 to the atmosphere while burning.

Biodiesel is usually synthesized by the reaction of C_{14}–C_{20} fatty acid tri-glycerides and short-chain alcohol (e.g., methanol or ethanol) in the presence of catalyst through the formation of di- and mono-glyceride intermediates. Vegetable oil, animal fat, algal and microbial oil are used frequently as feedstocks for biodiesel production. Rapeseed [5], Soybean [6–8], Sunflower [9–11], Canola [12], Palm [13] and Coconut [14] oils are the common edible oils for biodiesel synthesis; whereas Castor [15], Mahua [16], Karanja [3, 17] and Jatropha [18] are the major non-edible oils for biodiesel production. More recently, biodiesel production from Sal oil was also reported by Vedaraman et al. [19] using sodium hydroxide as a catalyst. Sulphuric acid, hydrochloric acid, sodium hydroxide, sodium methoxide, potassium hydroxide and potassium methoxide are the conventional homogeneous catalysts used for biodiesel production. The drawbacks of using these catalysts for biodiesel production are (1) the formation of corrosive environment during transesterification (2) poor recovery of the catalyst, (3) the requirement of additional purification steps to obtain the desired grade of

biodiesel, (4) huge amount of effluent generation and (5) the reduction of biodiesel yield due to additional purification steps [14, 20–22]. To overcome these difficulties, researchers used heterogeneous catalyst which was recycled easily with negligible generation of the effluents. Common heterogeneous catalysts for biodiesel synthesis are zeolites [23], alumina-loaded compounds [24], modified dolomites [25], ion-exchange resins [26, 27], potassium fluoride/hydrotalcite [28], calcium oxide [29] magnesium oxide-supported potassium hydroxide [30] and sodium aluminates [31]. In addition to these heterogeneous catalysts, the use of lipase-based enzyme has also been reported for transesterification reaction [32]. A catalyst-free production of biodiesel using supercritical alcohol has also been reported at elevated temperatures and pressures [26]. Moreover, biodiesel production was complicated in the presence free fatty acid (FFA) in oil [20, 22]. In this case, FFA content in oil was first esterified into the fatty acids of methyl ester (FAME) using methanol and sulphuric acid catalyst to reduce FFA content in oil. The reduced FFA oil was purified by removing moisture, sulphuric acid and excess methanol. Now, fatty acid-free tri-glycerides were converted into FAME by the conventional method of transesterification technique. Ghadge and Raheman [20] adopted above two-stage process to produce biodiesel from Mahua oil with high FFA content. Similarly, Naik et al. [22] converted high FFA content Karanja oil to biodiesel by two-stage process. Though the two-stage method can handle high FFA in oil very well, it requires additional processing steps to remove acid catalyst, moisture and alkali which adversely affect the production of biodiesel.

Sal tree (*Shorea robusta*) is native to southern Asia (i.e., India, Myanmar, Nepal, and Bangladesh) and it is widely distributed in tropical regions of India which covers about 13.3 % of the total forest area in the country. Sal is the source of one of the most important commercial timbers which are used for railway sleeper, beams, scantlings, floors, piles, bridges, carriage and wagon-building, shipbuilding industry, ladders, carts, spokes, hubs of wheels, tool handles, ploughs, dyeing vats, beer, oil casks and tanning materials. Sal resins are also widely used for the hardening of softer waxes for the use in shoe-polishes, carbon papers, typewriter ribbons, etc. It is also used as an ingredient of ointments for skin diseases and in ear troubles. Except for the work of Vedaraman et al. [19], there is very limited information available to produce biodiesel using Sal oil. Moreover, the use of ion-exchange resin catalyst was limited to the synthesis of biodiesel. In this study, a single-stage synthesis of Sal oil methyl ester (SOME) was explored using INDION 225 H catalyst (an acidic ion-exchange resin) and Sal oil with free fatty acids.

Materials and method

Materials

Sal (*Shorea robusta*) oil was collected from a rural area of Ranchi (Jarkhand, India) and was analysed for saponification value, iodine value and acid value. Specific gravity, kinematic viscosity, pour point, flash point and initial boiling points were also determined for the given specimen of Sal oil. INDION 225 H [supplied by Ion Exchange (India) Limited, Ankleshwar, India], an acidic solid ion-exchange resin catalyst was used for both esterification and transesterification reactions. Synthetic grade of sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium chloride (NaCl), anhydrous sodium sulphate (Na_2SO_4), hydrochloric acid (HCl), methanol and oxalic acid were supplied by Merck (Mumbai, India) for SOME biodiesel production and analysis. Petroleum-based diesel fuel was obtained from local petrol/diesel retailing station (Dhanbad, India) for the comparison of the properties of SOME biodiesel.

Characterization of ion-exchange resin catalyst

INDION 225 H ion-exchange resin catalysts are golden yellow and spherical in nature. The properties of resin catalysts (fresh as well recycled) were determined using standard tests [33]. Average particle size was measured using the traditional sieve analysis. Ion-exchange capacity was determined by passing 1 % NaCl solution through a bed of catalyst column. HCl was eluted out and the concentration was determined by the titration with NaOH, giving the ion-exchange capacity of the resin in meq/g. Porosity was determined by soaking the resin samples in water under vacuum. The difference between the dry and wet weight resin sample will result the porosity. Specific surface area of resin particles were measured by nitrogen adsorption using microflow BET technique (Model: NOVA 3200e, Quantachrome, UK). Morphological analysis of ion-exchange resin samples were performed using SEM (Model: FESEM-Carl Zeiss, Supra-55 VP and SDD X MAX 50 EDS, UK). Energy-dispersive X-ray spectroscope (EDX) analysis using SEM was also carried out for elemental analysis of the fresh resin catalyst. Ion-exchange capacity, SEM imaging and EDX analysis of the recycled catalyst were also carried out to check the activity and mechanical-cum-thermal degradation of the recycled ion-exchange resin catalysts.

Single-stage synthesis of SOME biodiesel

An experimental set-up for SOME biodiesel synthesis was proposed to remove moisture continuously to reduce the formation time of biodiesel with minimal usage of catalyst.

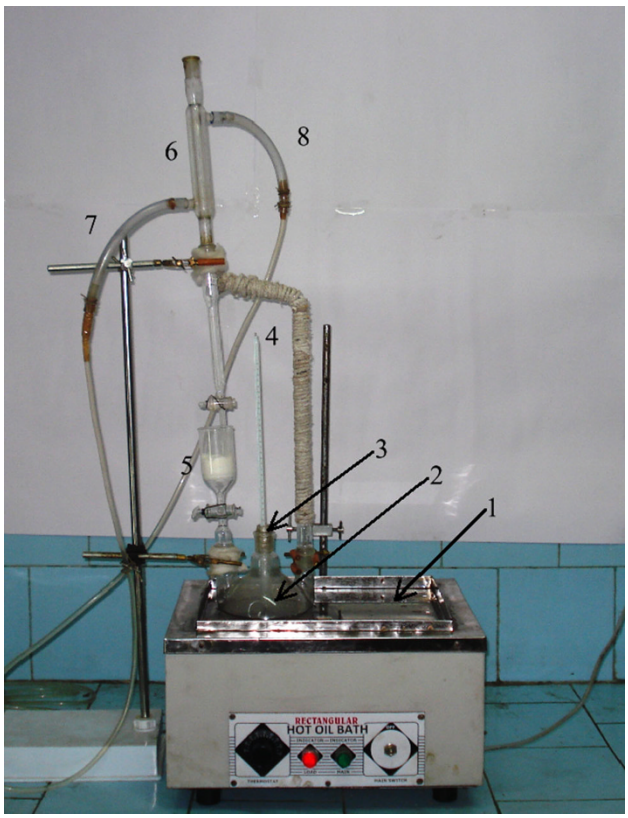

Fig. 1 Experimental setup for the production of biodiesel using INDION-225 H acidic ion-exchange resin catalyst: *1* hot oil bath, *2* reactor, *3* thermometer pocket, *4* Dean-Stark assembly, *5* sodium sulphate column, *6* overhead condenser, *7* cooling water inlet and *8* cooling water outlet

Effect of methanol and catalyst loading studies was carried out for fixing the best process parameters which will help to maximize the conversion of Sal oil to SOME biodiesel. To produce SOME biodiesel from Sal oil in a single step, an experimental set-up with moisture removal facility was made and the details are shown in Fig. 1. In this set-up, three-neck round-bottom flask was used, which was fitted with overhead Dean Stark assembly with reflux condenser, thermometer pocket and anhydrous bed of Na_2SO_4. To avoid moisture contamination and overheating, hot oil bath was used for heating. Methanol vapour was condensed from the overhead condenser and condensed methanol was passed through the Na_2SO_4 bed for dehydration. Dehydrated methanol was continuously fed to the reactor (Fig. 1) to make constant volume batch reactor. Hydrated Na_2SO_4 may also be reused after vacuum drying at 80 °C. Reacted samples were collected at regular intervals of time to check the acid value of the reaction mass and the reaction was continued until the acid number of the reaction mixture reached the acceptable limit of biodiesel (i.e., below 0.5 mg KOH/g oil). Ion-exchange resin catalysts were recycled for several times and the productivity of SOME biodiesel was tested with the recycled catalyst. Activity of recycled ion-exchange resin catalysts were also determined by checking the ion-exchange capacity of the recycled resin bead. Mechanical-cum-thermal degradation of the recycled resin catalysts was tested using scanning electron microscope (SEM) analysis and energy-dispersive X-ray spectroscope (EDX) analysis. In the proposed process, ion-exchange resin catalyst not only helps to reduce the consumption of catalyst and the effluent generation considerably but also enhances the productivity of SOME biodiesel substantially by eliminating the purification steps (for example, neutralization of base/acid, moisture removal, filtration of the precipitated salts and water washing to adjust acid value). In this study, mechanical stirring was avoided to reduce attrition of resin particles. It is mentioned that the reaction in the presence of excess methanol takes place at the boiling point of reaction mass and ensures the complete mixing. The loss of methanol was avoided by providing proper insulation in reactor-condenser assembly and sufficiently high cooling water flow rate in the condenser when reaction was carried out at the boiling point. This study is quite general and can be applied for biodiesel production from the varieties oils with high free fatty acids.

Purification of SOME biodiesel

After attaining the desired value of acid number, reaction mass was cooled to room temperature and filtered to recover ion-exchange resin catalyst. Recovered catalysts were directly used for the next cycle of biodiesel production. Filtrate was kept in a separating funnel for layer separation and glycerol was recovered from the bottom of the funnel. Water-washing of the top layer was not carried out, as pH of the reaction mass was within the desired limit. Moreover, oil–water emulsion formation was eliminated without using water washing in the present methodology. Distillation was carried out for the top layer to recover methanol. Finally, SOME biodiesel was recovered under

Table 1 Characteristics of INDION 225 H (an acidic ion-exchange resin) catalyst

Shape	Spherical
Colour	Golden yellow beads
Bulk density, kg/m^3	780
Average bead size, m	0.0048
Porosity, %	~52.0
Total ion-exchange capacity, meq H^+/g	5.5
Specific surface area, m^2/g	18–20
Effective operating pH	0–14
Temperature stability, °C	120

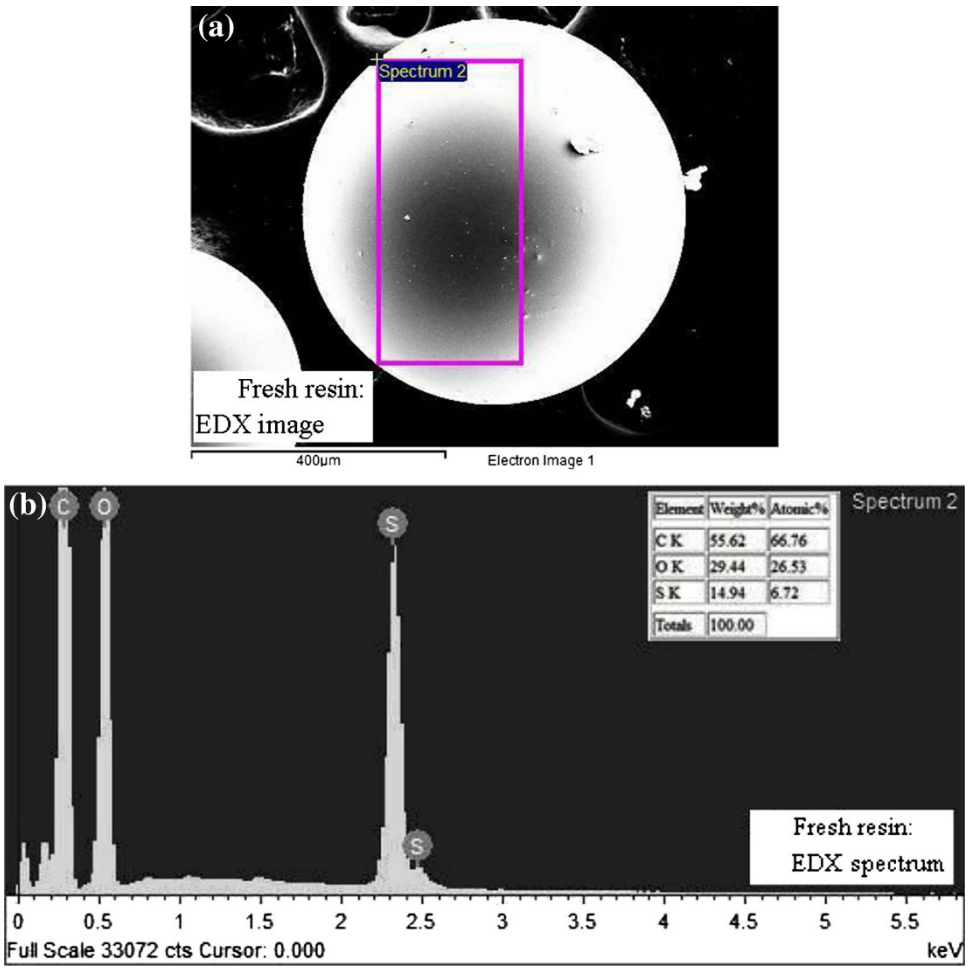

Fig. 2 Energy-dispersive X-ray spectroscope (EDX) spectrum of the virgin ion-exchange resin catalyst (INDION 225H)

full vacuum and the vacuum distillation was continued until the residue temperature reached 250 °C. It was noticed that a very negligible amount of residue was left after vacuum distillation which ensured the minimum loss of biodiesel. Finally, the properties of SOME biodiesel were determined using ASTM standard methods [34] and these properties were compared with the petroleum-based diesel fuel.

Characterization of SOME biodiesel

Important properties for biodiesel are kinematic viscosity, pour point, flash point, initial boiling point, final boiling point, gross calorific value and cetane number. Kinematic viscosity (ASTM D445) was measured using Cannon–Fenske viscometer at 40 °C. Pour point and flash point were measured as per ASTM D97 and ASTM D93 method using manual pour point and Cleveland open cup apparatus, respectively. Initial and final boiling points for SOME biodiesel were obtained by distillation method (ASTM D86) using electrically heated distillation apparatus assembly. Gross calorific values and cetane numbers were obtained from bomb calorimeter (Model: LECO, AC 350, UK) and portable MID/NIR-FTIR spectrometer (Model: ERASPEC: eralytics GmbH, Austria), respectively. Composition of FAME in SOME biodiesel was analysed by gas chromatograph (Chemito GC 8,610) with a SGE forte GC capillary column (BPX 70, 25 m × 0.53 mm × 0.5 µm). Temperatures of column, injector and detector ports were maintained at 230 °C, 24 °C and 280 °C, respectively, during analysis.

Statistical analysis

Biodiesel synthesis from Sal oil using ion-exchange resin catalyst was assessed by the analysis of variance (p). It was confirmed that the values of 'p' for 'acid values' were *almost* less than 0.02, whereas 'p' values for biodiesel yield were found to be less than 0.01.

Results and discussion

Catalyst properties

Properties of INDION 225 H ion-exchange resin catalysts (i.e., average particle size, ion-exchange capacity, porosity

Table 2 Properties of Sal oil, standard diesel oil and SOME biodiesel using ASTM method

Properties	Test method fossil diesel	Biodiesel standard, ASTM D6751 (limits)	Sal oil	Standard fossil diesel	SOME biodiesel
Saponification value, mg KOH/g oil	D94	–	198.3	–	194.2
Iodine value, g Iodine/100 g oil	D1959	–	49.2	–	46.7
Acid value, mg KOH/g oil	D664	0.5 maximum	1.20	0.30	0.18
Specific gravity @ 15 °C	D1298	–	0.879	0.82	0.875
Kinematic viscosity, cSt @ 40 °C	D445	1.9–6.0	45.0	3.0	4.8
Water content, % volume	D2709	0.050 maximum	0.0	0.01	0.02
Pour point, °C	D97	–	38	–16	18
Flash point, °C	D56	93.0 minimum (D93)	238	72	160
Initial boiling point, °C	D86	–	556	140	271
Final boiling point, °C	D86	–	–	355	339
Distillation temperature, 90 % recovered (T90), °C	D86	360 maximum (D1160)	–	343	330
Calorific value, kJ/kg	D240	–	–	43,502	39,870
Cetane number	D613	47 minimum	–	44	53
Free glycerin, % mass	D6584	0.020	–	–	0.01
Total glycerin, % mass	D6584	0.240	–	–	0.10

and surface area) were determined and details are given in Table 1. Elemental analysis of ion-exchange resin catalyst was also carried out using SEM-EDX and the detail of EDX spectrum and corresponding analysis is given in Fig. 2a and b, respectively. EDX analysis shows peaks caused by X-rays given off as electrons return to the K electron shell (Fig. 2b). It is observed that the atomic percent of oxygen and sulphur was found to be 26.53 and 6.72 %, respectively, and corresponding atomic ratio was calculated to almost 3.0. This reveals the presence of sulphonic acid group in the resin bead.

Characteristics of Sal oil

Properties of Sal oil (saponification value, iodine value, acid value, specific gravity, kinematic viscosity, water content, pour point, flash point and initial boiling point) were determined and details are given in column 4 of Table 2. The saponification value of oil gives an indication of the average molecular weight of fatty acids, while the iodine value gives a relative measure of the degree of unsaturation in fatty acids. The saponification value of Sal oil was found to be 198.3 mg KOH/g oil and, therefore, the average molecular weight of fatty acids is calculated as 282.4 g/mol [35] and it is closer to the molecular weight of stearic and/or oleic acid which was supported by FAME analysis of purified SOME biodiesel (Table 3). Similarly, iodine value of Sal oil was found to be 49.2 g iodine/100 g oil and acid value with 1.2 mg KOH/g oil indicates that Sal oil has negligible quantity of free fatty acids.

Important parameters that influence the productivity of SOME biodiesel are catalyst loading, methanol loading and catalyst recycling. As the reaction was carried out under atmospheric pressure with excess amount of methanol, the reaction temperature will be at the boiling point of the reaction mass.

Effect of catalyst loading

Catalyst loading has a marked effect on esterification of FFA and transesterification of fatty acid tri-glycerides of Sal oil. Five different catalyst loadings (i.e., 2.0, 5.0, 10.0, 15.0 and 20.0 % g catalyst/g Sal oil) were considered in the present study and molar ratio of Sal oil to methanol was kept constant at 1:12 for *all* the catalyst loading experiments. INDION 225 H ion-exchange resin is an inexpensive catalyst (~1.5 US$/kg) and it is always desirable to obtain maximum biodiesel yield using highest possible catalyst loading which depends on catalyst suspension ability under normal boiling condition. It was

Table 3 Fatty acid composition in SOME biodiesel

Fatty acids methyl ester	Molecular weight	Weight % of SOME biodiesel
Palmitic	270.45	5.1
Stearic	298.51	45.2
Arachidic	326.56	4.8
Oleic	296.49	43.1
Linoleic	294.47	1.8

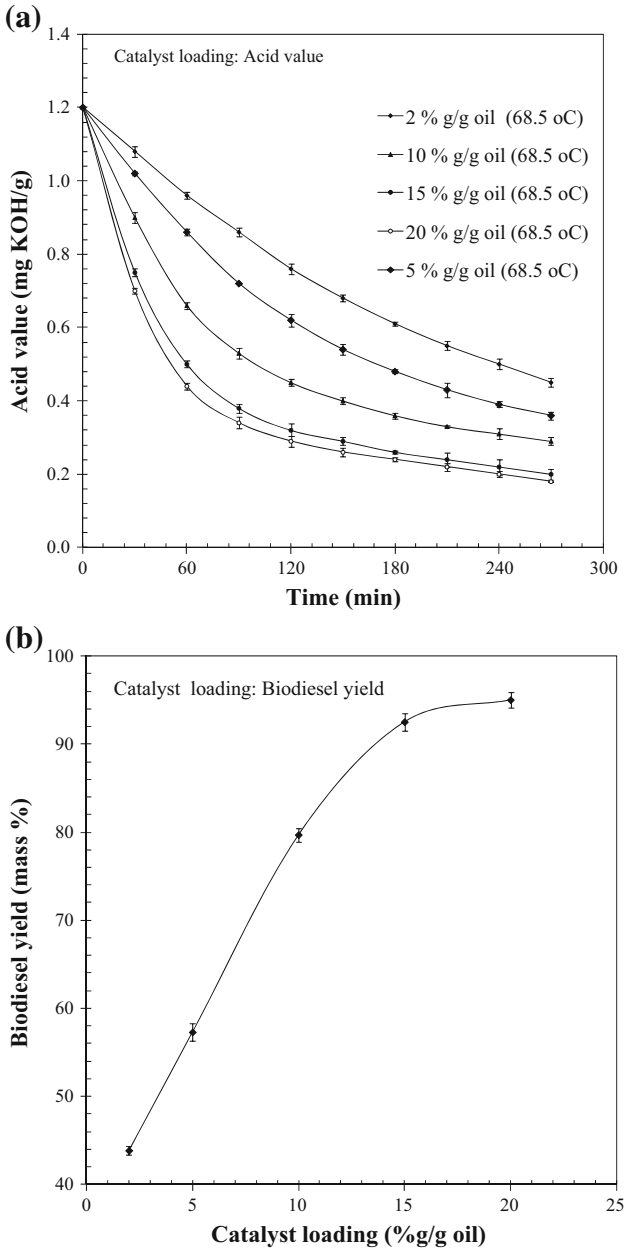

Fig. 3 **a** Effects of catalyst loading on lowering of acid values during reaction and **b** effects of catalyst loading on the yield SOME biodiesel

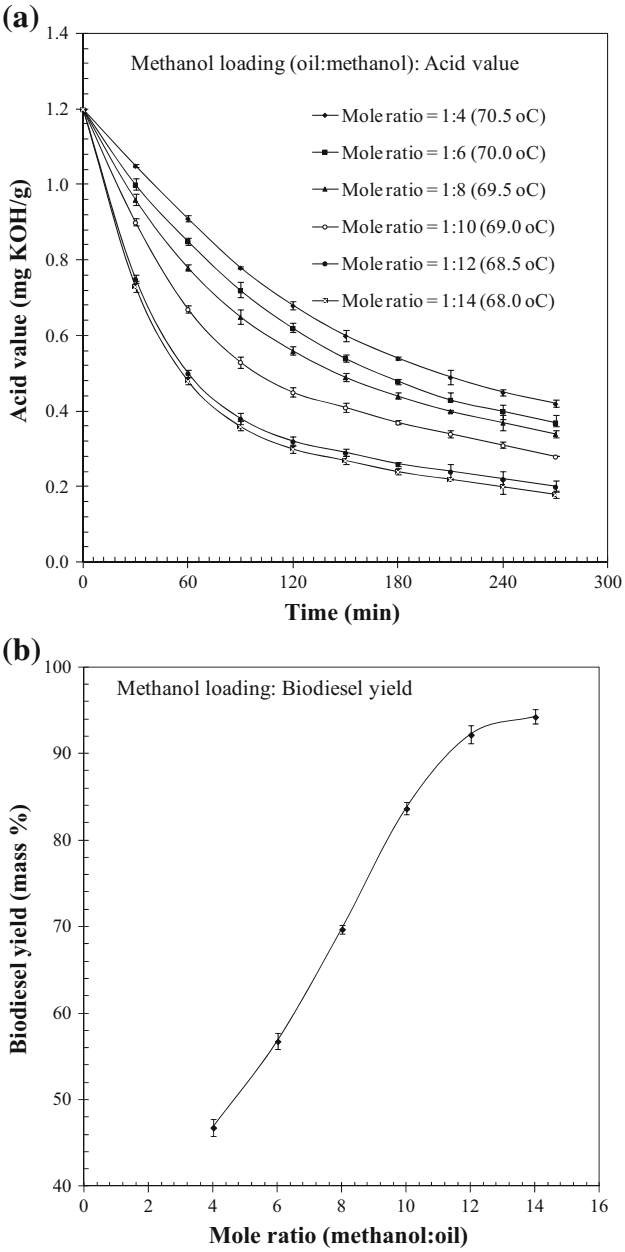

Fig. 4 **a** Effects of methanol loading on lowering of acid values during reaction and **b** effects of methanol loading on the yield SOME biodiesel

found experimentally that the settling of ion-exchange resin catalyst was absent at 20 % catalyst loading when the reaction was carried out at the normal boiling point. Therefore, maximum catalyst loading for SOME biodiesel synthesis was fixed at 20.0 %. The acid value of the reaction mixturedeclines sharply with increase in catalyst loading and the time required to achieve the limiting acid value of biodiesel (i.e., 0.5 mg KOH/g oil) was maximum for 2.0 % catalyst loading (lowest catalyst loading), which was found to be 270 min (Fig. 3a). Therefore, in subsequent experiments with increasing catalyst and methanol loading, reaction time was kept at 270 min. The variations of acid value with the time of reaction using different catalyst loading are shown in Fig. 3a. It was also noticed that the reduction of acid value using 20.0 % catalyst loading is *almost* similar to 15.0 % catalyst loading (Fig. 3a). It was observed that acid value of the reaction mass was reduced below 0.5 mg KOH/g oil at a faster rate for higher catalyst loadings (i.e., 15.0 and 20.0 %) as compared to lower catalyst loading. Also the reduction of acid value using 20.0 % catalyst loading is almost similar to 15.0 % catalyst loading (Fig. 3a). The

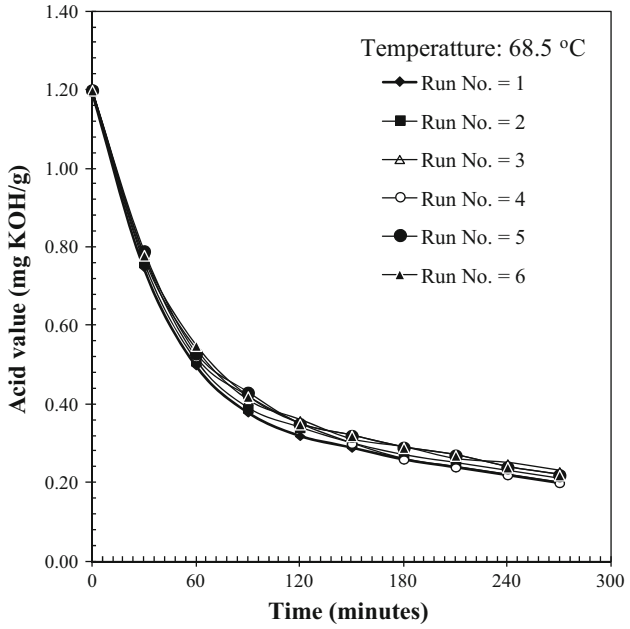

Fig. 5 Effects of catalyst recycling on the lowering of acid values during reaction

details of SOME biodiesel yields for *all* the catalyst loading experiments are given in Fig. 3b. It was noted that the yield of biodiesel was obtained more than 90 % for 15.0 and 20.0 % catalyst loading. Therefore, catalyst loading for the subsequent experiments was fixed at 15.0 % (g catalyst/g Sal oil). Vedaraman et al. [19] also carried out the synthesis of SOME biodiesel using sodium methoxide catalyst. Biodiesel synthesized in the present study using INDION 225 H ion-exchange resin catalyst was compared with SOME biodiesel yield which was obtained using sodium methoxide catalyst [19]. An almost 95.0 % yield of SOME biodiesel was obtained using ion-exchange resin and sodium methoxide catalyst when acid value of purified biodiesel was below 0.5 mg KOH/g oil. Though the requirement of ion-exchange resin catalyst for given biodiesel yield was comparatively higher than the studies of Vedaraman et al. [19], but overall specific consumption of ion-exchange resin catalyst was almost negligible due to complete recycle of the catalyst with minimum effluent generation. It was also noted that the yield of SOME biodiesel was less than 100 % for all catalyst loading experiments, which suggests the presence of tri-, di- and mono-glycerides in the reaction mixture at the end of the reaction.

Effect of methanol loading

Effect of methanol loading on SOME biodiesel synthesis was carried out to select the optimum loading of methanol during esterification and transesterification reaction. Usually, low methanol loading increases the reaction time, whereas high methanol loading reduces the net output of biodiesel production for given batch size. Six different methanol loading experiments with different molar ratio of Sal oil to methanol (i.e., 1:4, 1:6, 1:8, 1:10, 1:12 and 1:14) were considered. The variations of acid value with reaction time are shown in Fig. 4a and corresponding yields of SOME biodiesel are shown in Fig. 4b. It was observed that the best results (i.e., minimum reaction time and maximum biodiesel yield) were obtained for the experiments with molar ratio of 1:12 and 1:14. Due to the marginal improvement in acid value of the reaction mixture and SOME biodiesel yield, the best methanol loading was selected as 1:12 molar ratio of Sal oil to methanol which is equivalent to 300 % of excess methanol by volume (Fig. 4a, b). At this molar ratio, biodiesel yield was found to be almost 93.0 % when acid value of the reacted mass was just below 0.5 mg KOH/g oil and similar results were also reported by Vedaraman et al. [19], where reaction time was much higher as compared to the present studies (Fig. 4a).

Effect of catalyst recycling

To reduce the cost of SOME biodiesel, it is necessary to recycle the ion-exchange resin catalyst. For catalyst recycling, all experiments were carried out at the optimum operating conditions (i.e., catalyst loading: 15.0 % g catalyst/g Sal oil and Sal oil to methanol molar ratio 1:12). The variations of acid value with reaction time using recycle catalyst for six consecutive studies are shown in Fig. 5. It was noted that acid value vs. reaction time pattern using recycled INDION 225 H ion-exchange resin catalyst is almost similar and corresponding SOME biodiesel yield is almost 91.0 % for all the recycle runs. To check the mechanical-cum-thermal degradation of the ion-exchange catalyst, SEM analysis was carried for all the recycled catalysts and SEM images were compared with fresh ion-exchange resin catalyst. Details of resin morphology using SEM for all the recycled catalyst samples are shown in Fig. 6a–g. It was observed that none of the ion-exchange resin catalyst had been degraded after sixth recycle. A layer of the reaction products was observed on the catalyst surface after first recycle and gradually the layer increases as the number of catalyst recycling increases. Though the layer on catalyst surface increases with the number of recycles, still the reactivity of the resin catalyst was almost unaffected with number of recycles (Fig. 5). The unchanged activity of resin is mainly due to the smoothness of resin surface after several recycles which is visible through the product layer (ref. SEM micrographs: Fig. 6a–g). The activity of the recycled resin catalyst was determined and ion-exchange capacity after sixth recycle was found to be

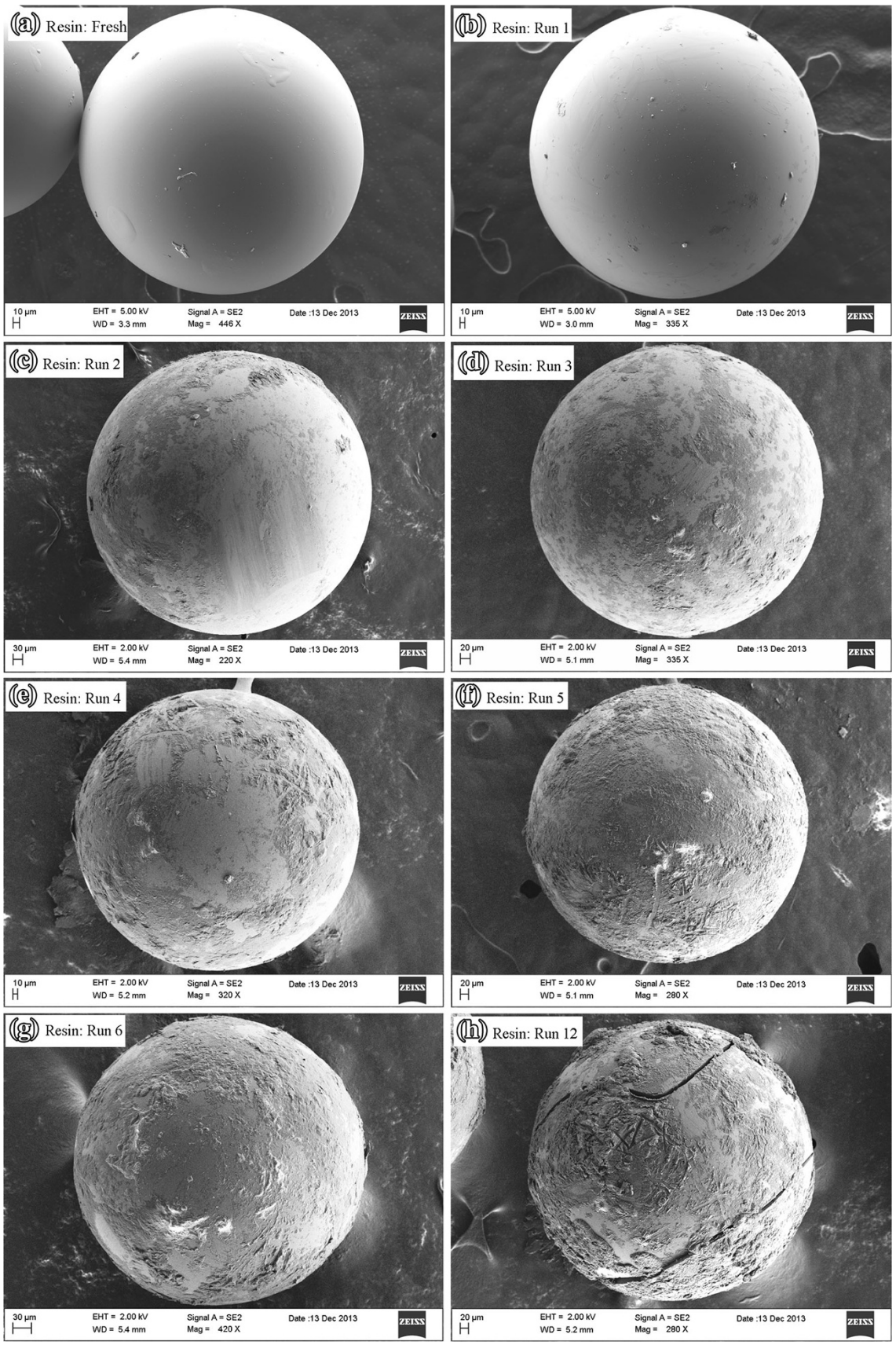

Fig. 6 Scanning Electron Microscope (SEM) images of the recycled ion-exchange resin catalysts (Runs 1–6 and 12)

5.5 meq H^+/g of catalyst which is exactly the same as the fresh resin catalyst (Table 1). The same catalyst (i.e., after sixth recycle) was also used for biodiesel synthesis. A constant SOME biodiesel yield was obtained for all the recycle runs (i.e., Run no. >6). During the recycle experiments, a mini crack was observed on the catalyst surface after 12 recycles which was confirmed by SEM image (Fig. 6h). This indicates that the ion-exchange resin can be recycled for 12 times without mechanical-cum-thermal degradation. Reaction was also carried out further with the degraded resin catalyst (i.e., after twelve recycle) and it was found that the yield of SOME biodiesel also remains unchanged using degraded resin catalyst. As number of recycle (>twelve recycle) increases, degradation of resin particles are also increased, producing more catalyst fines which is difficult to recover and recycle for biodiesel synthesis.

To identify the layer on the catalyst surface for all the recycle runs, SEM image analysis was carried out for sixth run catalyst sample with layer (Run 6). Details of SEM image of catalyst particle with layer are shown in Fig. 7a and corresponding enlarged SEM image is shown in Fig. 7b. EDX analysis for this catalyst was carried out for the layered surface only (i.e., excluding resin matrix) and corresponding results are shown in Fig. 7c, d. It shows peaks caused by X-rays given off as electrons return to the K electron shell (Fig. 7d). From EDX analysis (Fig. 7d), carbon to oxygen atomic ratio is found to be 6.74 and it corresponds to a mixture of glycerol and SOME biodiesel whose carbon to oxygen atomic ratio is 1.0 and ~9.5, respectively.

Testing of SOME biodiesel

The Sal oil biodiesel synthesized using INDION-225 H ion-exchange resin was tested as per ASTM method of analysis and compared with petroleum-based diesel fuel. Details of petroleum-based diesel fuel and SOME biodiesel properties are listed in columns 4 and 5 of Table 2, respectively. Saponification and iodine values depend on the number of fatty acid molecules and unsaturated double bonds in the fatty acids. Conventional field units of the measured properties of biodiesel have been retained in Table 2 for comparison. The acid value of all the all biodiesel samples were found to be ~0.2 mg KOH/g oil which is less than petroleum-based diesel fuel. Comparable values of specific gravity and kinematic viscosity were obtained for SOME biodiesel and petroleum-based diesel fuel. Calorific value of SOME biodiesel was found to be lower than the petroleum-based diesel which is mainly due to higher oxygen content in biodiesel. Average flash point of SOME biodiesel was found to be 160 °C which is also higher than the conventional diesel fuel which is mainly due to high average molecular weight SOME biodiesel. Similarly, average pour point of SOME biodiesel was found to be 18 °C which is also higher than the conventional diesel fuel. Average initial boiling point and final boiling point of SOME biodiesel were found to 258 and 335 °C, respectively. Cetane number for SOME biodiesel was found to 53 which are also higher than petroleum-based diesel fuel. Similarly, water content, total glycerin and free glycerin was also determined, and these values were found to be acceptable within the desired limits (Table 2). Details of the ASTM distillate temperature variation with percent recovery of SOME biodiesel are shown in Fig. 8 and results are also compared with standard petroleum-based diesel fuel. It is observed that the distillation pattern for the SOME biodiesel is almost flat at the middle of the distillation process. The constant temperature flat distillation profile may be advantageous for uniform combustion of SOME biodiesel in diesel engine. The distillation pattern of SOME biodiesel differs from the standard petroleum-based diesel fuel and the difference is mainly due to narrow molecular weight distribution of SOME biodiesel as compared to petroleum-based diesel fuel [36]. Fatty acid composition of SOME biodiesel was also determined by GC analysis and details are given in Table 3. The analysis shows that Sal oil is composed of 'fifty-fifty' mixture of stearic and oleic acid which is also similar to the studies reported by Vedaraman et al. [19].

Conclusion

An optimal synthesis of methyl ester of Sal oil biodiesel was carried out using INDION 225 H ion-exchange resin catalyst. An experimental set-up was proposed to synthesize Sal oil biodiesel where esterification and transesterification occurs simultaneously with continuous removal of water. Effect of catalyst and methanol loading studies on biodiesel yield was carried out to select the optimal operating parameters. Optimum catalyst and methanol loading was found to 15.0 % g catalyst/g Sal oil and 1:12 molar ratio of Sal oil to methanol, respectively. In this process, resin catalyst was recycled and the yield of Sal oil biodiesel was unaffected after the recycling of catalyst for several times with negligible effluent generation. Mechanical-cum-thermal degradation of ion-exchange resin catalyst was verified using SEM study and results show that catalyst starts degradation with mini cracks after the twelfth recycle with a layer of reaction products, which was confirmed by EDX analysis. Sal biodiesel was purified under vacuum and tested using the standard ASTM method of product testing. Comparable properties (e.g., acid values, specific gravity, kinematic viscosity, pour point, flash point, initial boiling point, final boiling point, calorific value and cetane

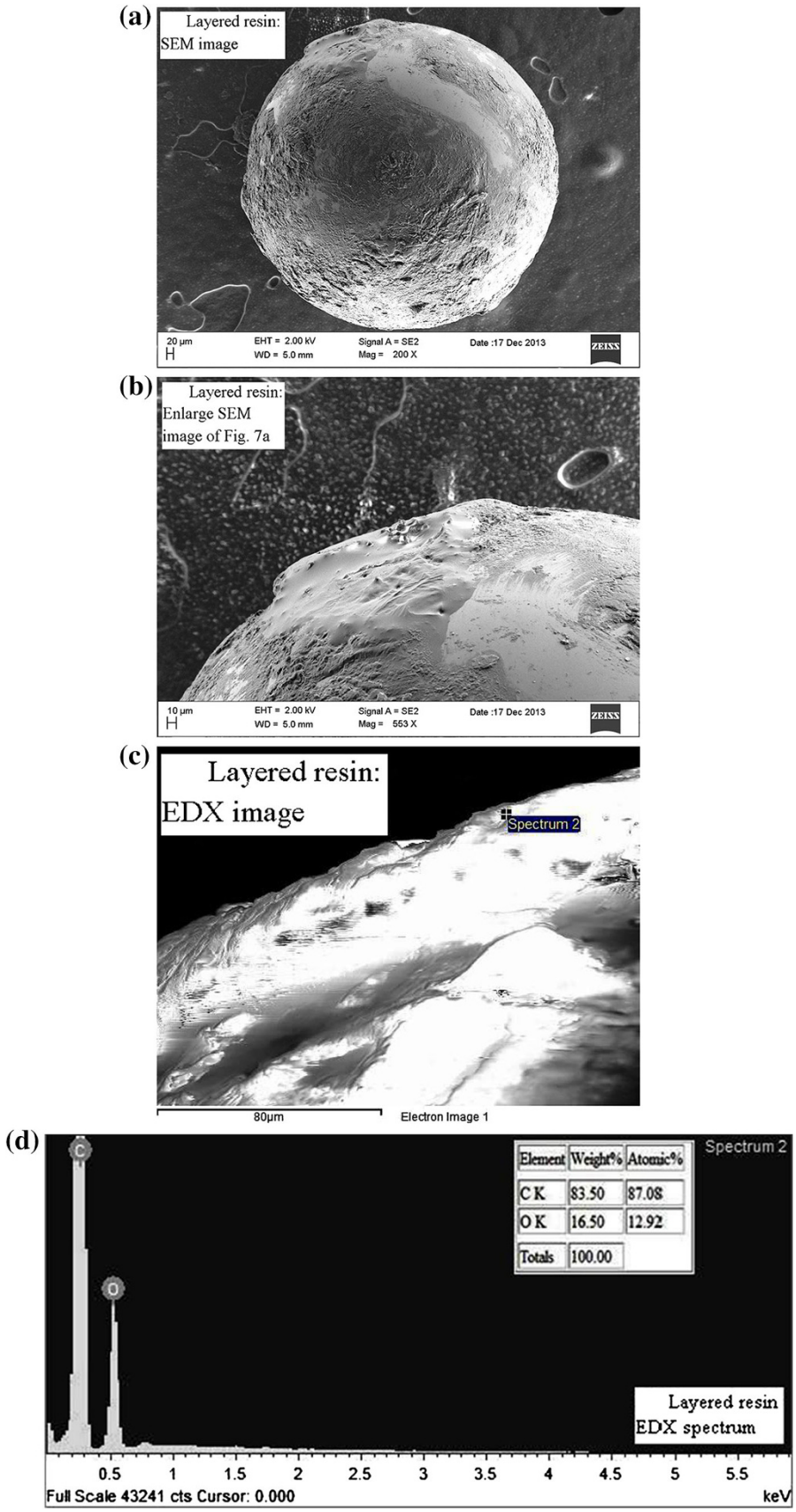

Fig. 7 Analysis of the deposited layer on the recycled resin catalyst surface (Run 6): **a** SEM image, **b** enlarged SEM image of **a**, **c** EDX image and **d** EDX spectrum of (**c**)

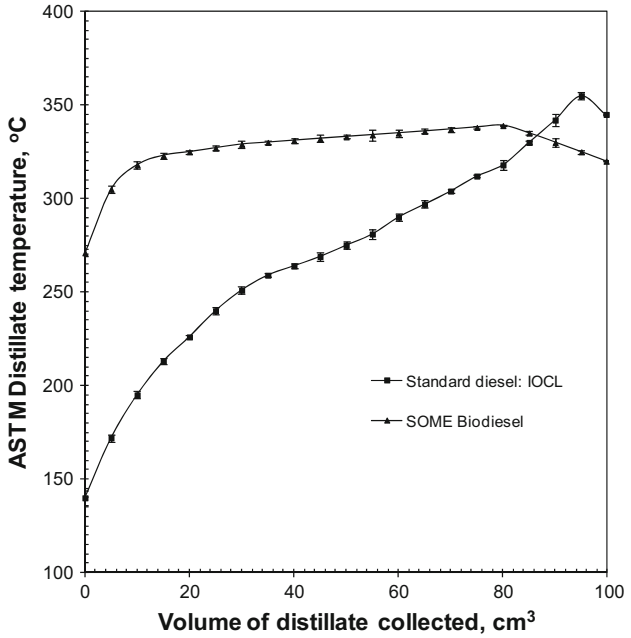

Fig. 8 Per cent distillate recoveries with distillate temperature for SOME biodiesel and standard petroleum diesel fuel under ASTM distillation

number) of Sal biodiesel were obtained with respect to petroleum-based diesel fuel. The present method of single-stage synthesis of biodiesel may be extended for the oils with high free fatty acids through monitoring tri-, di- and mono-glycerides.

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